

## THE INFLUENCE OF CARBONACEOUS ADDITIVES ON MESOPHASE FORMATION FROM ATHABASCA BITUMEN

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### ABSTRACT

The effect of carbonaceous additives (soot and coke) on the mesophase induction period, growth and coalescence of Athabasca bitumen vacuum bottoms fraction was investigated using hot-stage microscopy. Two types of soot materials and coke from a delayed coking operation at Fort McMurray, Alberta were used in this study. The soot #1 additive did not have a pronounced effect on the mesophase induction period and growth whereas soot #2 additive prolonged the induction period and resulted in very small mesophase (2-4 $\mu$ m) after 120 min. The results were rationalized in terms of the physical interaction between the soot particles and the mesophase spheres. Addition of coke resulted in the shortening of the mesophase induction period and the formation of relatively larger domains.

### INTRODUCTION

During bitumen upgrading by thermal treatment for the production of synthetic crude oil, an undesirable by-product known as coke which is insoluble in most organic solvents is formed. Coke formation is believed to be the result of physical and chemical processes. In the process leading to coke formation, phase separation (Cartlidge et al. 1996) and asphaltenes flocculation (Storm and Sheu 1996) are known to occur initially. These occurrences are followed by chemical reactions such as radical polymerization and/or cyclization/dehydrogenation reactions (McMillen et al. 1994). Prior to coke formation, an intermediate phase known as mesophase is formed. The initial time of mesophase formation is referred to as *induction period* which is strongly dependent on the chemical composition of feedstocks (Rahimi et al 1998). Petroleum residua rich in asphaltenes are expected to have a very short induction period (Wiehe 1993) whereas materials containing no asphaltenes generally show a longer but variable induction period for mesophase appearance (Rahimi et al. 1998). Prolonging the induction period during bitumen upgrading has important implications for the upgraders as shown below:

- 1- Provides longer operation between scheduled shutdowns
- 2- Results in higher liquid yields (less coke)
- 3- Leads to a more efficient plant operation
- 4- Results in less GHG emissions

During thermal conversion of petroleum residua containing asphaltenes to distillable liquid products, an induction period prior to coke formation has been observed by numerous investigators. Prolonging the induction period has been attempted in a number of ways, such as the addition of a hydrogen donor (H-donor) to the feed, the addition of an aromatic gas oil, or the introduction of a donor-refined bitumen in

a pretreatment step (Speight 1999). Using hot-stage microscopy, the effect of a clay additive (kaolinite) on the mesophase induction period during the thermal treatment of Athabasca bitumen was studied at the National Centre for Upgrading Technology (Rahimi et al. 1999). The results showed that there was a small or no effect on the induction period. In the presence of kaolinite the size of mesophase was significantly smaller compared with the experiments where no additive was used. Furthermore, the work by Tanabe and Gray (1997) on the thermal hydrocracking of Athabasca bitumen vacuum bottoms at a relatively short reaction times (20-30 min) using an autoclave showed that the presence of solid additives also resulted in a 7-9wt% reduction in coke yield.

The objective of this study was to investigate the effect of solid carbonaceous additives such as soot and coke on the mesophase induction period during the thermal treatment of Athabasca bitumen vacuum bottoms.

## EXPERIMENTAL

The Athabasca bitumen vacuum bottoms fraction (ABVB) used in this study was obtained by super critical extraction using pentane (Rahimi et al. 1998). Soot #1 was obtained from Material and Electrochemical Research Corporation and used as received. Soot #2 was an experimental soot received from TDA Research and was extracted with toluene to remove the soluble portion prior to use. The coke sample used in these experiments was obtained from a delayed coking operation in Alberta.

The mixtures of additives and bitumen fraction were prepared first by dissolving bitumen in methylene chloride, then adding the appropriate concentration of soot #1 at 1wt%, soot #2 at 5wt% and coke at 5wt%, and then sonicating each mixture for 60 min. The mixtures were then allowed to dry under nitrogen stream and left in a vacuum oven at 60°C for 3h.

For hot-stage microscopy tests, small quantities of each mixture (5-10 mg) were placed in aluminum cups at the centre of the heated cell. The experiments were conducted in the presence of hydrogen atmosphere, at a flow rate of 35 mL/min. The gas pressure was 750 psi and the final temperature (dwelling temperature) was 440°C and 450°C. The rate of heating was kept constant at 11°C/min from room temperature to the desired temperature. For a detailed description of the experimental procedure, the reader is referred to Rahimi et al. (1998).

## RESULTS AND DISCUSSION

The descriptions of photomicrographs obtained from hot-stage microscopy experiments on ABVB without and with additives are given below and shown in Fig. 1a-d.

### ABVB fraction with no additive

The mesophase induction period ranged from 61 min at 450°C to 67 min at 440°C. Mesophase spheres formed, grew, and coalesced to produce large domains (Figure 1a). As was shown previously (Rahimi et al. 1998), in the presence of hydrogen gas, mesophase grew without restrictions. The formation of

mesophase from this solids-free residue may indicate that the presence of dispersed solids is not a prerequisite for the formation of anisotropic mesophase via the nucleation process as proposed by Tillmanns et al. (1978).

#### Mixture of ABVB with Coke

The mixture was characterized by a very short mesophase induction period: 45 min at 450°C and 53 min at 440°C. The sample appeared to be very reactive and fluid throughout the experiment. The results showed that, in contrast to the presence of clay additives (Rahimi et al. 1999), the presence of coke did not increase the viscosity of the isotropic matrix and did not restrict the movement of mesophase spheres. Mesophase was high viscoelastic and formed large optical domains (Figure 1b). The observed fluidity requires further investigation since it may be related to the role of the chemical composition of the coke (radical scavenging via hydrogen transfer).

It was further observed that in the early stages of the experiment, some mesophase disappeared in the isotropic matrix and reappeared shortly after which may indicate sinking and floating of the particle as its density changed relative to that of the isotropic matrix.

#### Mixture of ABVB with Soot #1

The mixture of the ABVB fraction and soot #1 at 1wt% resulted in the following mesophase induction period: 62 min at 450°C and 70 min at 440°C. These data indicate that the presence of soot at the above concentration did not have a significant effect on prolonging or shortening the induction period prior to mesophase formation. Mesophase spheres grew almost uninhibited and coalesced to form larger domains (Figure 1c). The observed mesophase texture shown in Fig. 1c is consistent with that reported by Matsumoto et al. (1977): the concentration of soot particles was too small to cover the surface of mesophase spheres completely. As a result the mesophase grew to form larger spheres.

#### Mixture of ABVB with Soot #2

The addition of soot #2 to the ABVB fraction resulted in a slight prolongation of the mesophase induction period. In this case, mesophase spheres first became visible at about 67 min at 450°C and 75 min at 440°C. The addition of this soot had a significant effect on the size, growth, and coalescence of mesophase and resulted in very small mesophase even after 120 min (Figure 1d). The apparent viscosity of this mixture was higher than the viscosity of bitumen-soot #1 mixture. This observation can simply be the result of the higher concentration of soot #2 used in the current experiment. As the concentration of soot increased from 1wt% to 5wt%, the size of mesophase became smaller and the size distribution more uniform because of the limited coalescence of the spheres (compare Figure 1c with Figure 1d).

Based on the above observations, it was concluded that the use of carbonaceous materials may have beneficial effects in terms of mesophase induction period (soot #2 additive) and in terms of possible chemical reactions that may reduce radical-radical combination (coke additive).

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## DESCRIPTION OF PHOTOMICROGRAPHS

All photos were taken in reflected light. The long axis of each photo is 300 $\mu$ m.

- Figure 1a: Formation of anisotropic mesophase spheres from the ABVB fraction in the absence of additives.
- Figure 1b: The presence of coke in the ABVB fraction resulted in the development of larger domain bulk mesophase in a highly fluid matrix.
- Figure 1c: Soot #1 did not influence the formation or the size of mesophase from the ABVB fraction.
- Figure 1d: The addition of Soot #2 to the ABVB fraction resulted in the formation of much smaller mesophase spheres than with either Soot #1 or coke.

Figure 1 – Mesophase formation in the absence and presence of coke and soot additive

